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TITLE : PRODUCTION OF FOAM HAVING DIRECTIONAL PORE

ABSTRACT : PROBLEM TO BE SOLVED: To inexpensively produce foams of high melting materials (metals and ceramics) having excellent lightness in weight, air permeability and filtration characteristic and directional pores.

SOLUTION: Metals or ceramics are melted in a melting furnace to obtain molten metal. Gases consisting of at least one kind of gases among gaseous H, N and O, are applied to this molten metal and the total pressure 1 to 500atm of the gases is applied thereto to dissolve the gases. Casting molds are preheated to a range of the respective m.p. of the metals or ceramics ±50°C. While the total pressure of the gases applied to the molten metal is maintained, the molten metal is poured into the preheated casting molds. While the total pressure of the gases applied to the molten metal is maintained, the heat extraction from the upper surface and flanks of the casting molds is prevented and the heat is extracted from the lower surface alone to allow the molten metal to solidify. The molten metal is unidirectionally solidified to the foam which extends upward, has the directional pores of a minor diameter of 5µm to 10mm and porosity of 50 to 98%. Further, fine particles to constitute the nuclei for foaming are added to the molten metal.

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(54)【発明の名称】 方向性気孔を有する発泡体の製造方法

(57)【要約】

【課題】 軽量性、通気性および遮断性に優れ、方向性気孔を有する高融点物質(金屑およびセラミックス)の発泡体を安価に製造する。

【解決手段】 工程(a)～(e)で製造する。(a)溶解炉内において金屑又はセラミックスを溶解し浴湯を得る。(b)浴湯に対してH₂、N₂及びO₂ガスの内1種以上のがスのみからなり、当該ガスの全圧力1～500気圧を加えガスを溶解させる。(c)鋳型を金屑又はセラミックスの各融点±50℃の範囲に予熱する。(d)浴湯に加えられたガスの全圧力を保持したまま、上記予熱された鋳型に浴湯を鋳込む。(e)浴湯に加えられたガスの全圧力を保持したまま、鋳型の上面及び側面からの抜熱を防止し、下からのみ抜熱をし、浴湯を凝固させ、上方に延びた短径5μm～10mmの方向性気孔を有し、且つ気孔率50～95%の発泡体に一方向凝固させる。更に、浴湯に発泡核となる微細粒子を添加する。

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【特許請求の範囲】

【請求項1】 下記(a)～(e)の工程よりなることを特徴とする方向性気孔を有する発泡体の製造方法。

(a) 溶解炉内において金属またはセラミックスを溶解して浴湯を得る工程、

(b) 次いで、前記浴湯に対して水素、窒素および酸素ガスの内少なくとも1種のガスのみからなり、当該ガスの全圧力を1～500気圧の範囲内で加えることにより、前記浴湯に前記ガスを溶解させる工程、

(c) 鋳型を、前記金属または前記セラミックスのそれぞれの融点-50°C以上、融点+50°C以下の範囲内の温度に予熱する工程、

(d) 次いで、前記浴湯に加えられた前記ガスの全圧力を保持したまま、前記温度に予熱された前記鋳型に、前記浴湯を詰込む工程、および、

(e) 前記浴湯に加えられた前記ガスの全圧力を保持したまま、前記鋳型の上面および側面からの抜熱を防止し、前記鋳型の下面からのみ抜熱をし、浴湯を凝固させることにより、上方に長く伸びた短径5μm～10μmの方向性気孔を有し、且つ気孔率5%～98%の発泡体に一方向凝固させる工程。

【請求項2】 請求項1記載の発明の工程に、更に、浴湯に発泡核となる微細粒子を添加する工程を付加することを特徴とする方向性気孔を有する発泡体の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 この発明は、発泡金属（合金を含む）および発泡セラミックスの製造方法に関するものである。

【0002】

【従来の技術】 発泡金属および多孔質セラミックスは、それぞれ、金属中に発泡による無数の気泡を残留させた金属の一様、およびセラミックス中に無数の気孔を形成させたセラミックスの一様であり、いずれも軽量で通気性および透過機能に優れた材料である。

【0003】 このような発泡金属を製造する方法として次の①および②の方法がある。

①電気メッキによる製造方法

この方法では、発泡樹脂としてウレタンフォームを使い、これに導電処理を施すためにカーボンを塗布し、これを電気メッキ槽の中でニッケルメッキを施す。ニッケルメッキ後は600°Cでばい焼して、ウレタンフォームを焼却し、更に、900°Cの水素気流中で還元する。発泡基材にピッチ系炭素繊維のフェルトを用いる場合は、ピッチ系炭素繊維が導電性であるから導電処理は不要であるが、上記例と同様に順次、フェルトの洗浄、電気メッキ、ばい焼まで還元の工程を経て製造される。

【0004】 このようにして得られた発泡金属を、Ni-Cd、Ni-H電池の電極の基板として用いると、Ni_{1-x}(OH)_xの正極活性質や、Cdや水素吸蔵合金等の

負極活性質を、気孔内に多量に充填することができるため、電池の小型化、高容量化を図ることができる。

【0005】 ②铸造法による製造方法

この方法は、アルミニウムのような融点の低い発泡金属の製造で採用されている。即ち、金属浴湯へ空気を吹き込み、カルシウム等を添加して粘度を増加させた後、その融点近傍の温度において発泡剤を添加する。発泡剤としては、ガスを発生する水素化物や、水を含む天然鉱物を用いる。金属浴湯に発泡剤を添加すると直ちにガス発泡が発生するので、鏡拌機で早く浴湯を鏡拌して気泡を分散させつつ凝固させる。

【0006】 一方、セラミックスの多孔質体を製造する方法としては、

③焼結法による方法がある。この方法は、セラミックスを所定の粒度範囲に調製し、得られたセラミックス粉末を焼結して製造するのが一般的である。

【0007】

【発明が解決しようとする課題】 しかしながら、上記①～③の製造方法には、それぞれ次の問題がある。即ち、①電気メッキによる製造方法は、上述したように多数の工程からなっている。従って、この方法で製造される発泡金属を薄くスライスして作られる発泡金属板は高価なものとなってしまうので、発泡金属の普及を妨げる一因になっていた。

【0008】 ②铸造法による場合には、発泡剤が比較的低い温度でガスを発生してしまうので、アルミニウムのような融点の低い金属しか製造することができず、ニッケルや鉄などのように1000°Cを超える高い融点を有する金属の発泡体製造は、これまで困難であった。また融点の高い金属の発泡体を製造する場合には、発泡剤としてチタン水素化物等のようにガス発生高温の高い物質を用いなければならない、ところがこのような発泡剤は高価であり、製造コストが高くなる。

【0009】 ③焼結法による発泡セラミックスでは、気孔率が50%程度のものしか製造することができず、軽量性および通気性に問題があった。従って、この発明の目的は、上述した問題を解決し、適切な製造工程により従来よりも安価に製造し、また従来は製造が困難であったり、発泡体が高価なため製造コストの高かった高融点の金属の発泡体を簡易な方法で製造し、より安価に製造する。そして、従来得られなかつた、軽量で通気性に優れた高性能な発泡セラミックスを簡便に製造することができる方法を提供することにある。

【0010】

【課題を解決するための手段】 本発明者等は、上述した観点から、全く新しい方法で、気孔の大きさおよび方向性、並びに気孔率を制御することができる発泡金属および発泡セラミックスを簡便に製造する方法を開発すべく鋭意研究を重ね、次の知見を得た。即ち、当該物質を溶融し、得られた浴湯に適切な高圧下でガスを溶解させ、

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ガスを溶解させたままの状態で溶湯を攪拌しながら冷却を制御しつつ凝固させることにより、希望する性状の発泡金属性および発泡セラミックスを製造することができるを見出した。

【0011】本発明は上記知見に基づきなされたものであって、請求項1記載の発泡体の製造方法は、下記(a)～(e)の工程よりなることに特徴を有するものである。

(a) 溶解炉内において金属またはセラミックスを溶解して溶湯を得る工程、(b) 次いで、溶湯に対して水素、窒素および酸素ガスの内少なくとも1種のガスのみからなり、当該ガスの全圧力を1～500気圧の範囲内で加えることにより、溶湯にガスを溶解させる工程、

(c) 鋳型を、金属またはセラミックスのそれぞれの融点-50°C以上、融点+50°C以下の範囲内の温度に予熱する工程、(d) 次いで、溶湯に加えられた全圧力を保持したまま、上記温度に予熱された鋳型に、溶湯を铸込む工程、および、(e) 溶湯に加えられたガスの全圧力を保持したまま、鋳型の上面および側面からの抜熱を防止し、鋳型の下面からのみ抜熱をし、溶湯を凝固させることにより、上方に長く延びた短径5μm～10μmの方向性気孔を有し、且つ気孔率5%～98%の発泡体に一方向凝固させる工程。

【0012】請求項2記載の発泡体の製造方法は、請求項1に記載の発明に、更に、溶湯に発泡核となる微細粒子を添加する工程を付加することに特徴を有するものである。

【0013】

【発明の実施の形態】次に、この発明の製造方法を上述した通り規定した理由を説明する。

(イ) 溶湯に対するガスの全圧力=1～500気圧の範囲内に保持し、且つその圧力を保持したまま、所定の鋳型に铸造し冷却し凝固させること：まず金属またはセラミックスを所定の方法で溶解し、次いで得られた溶湯に窒素、酸素および水素ガスの内少なくとも1種のガスを含み、その他のガスは実質的に含まれないガス雰囲気を作る。このガス雰囲気の全圧力が1～500気圧の範囲内で、当該ガスを溶解させる。ガスの全圧力が1気圧未満ではガスの溶解量が少なく、高い気孔率の発泡体を得ることが困難である。一方、500気圧までの全圧力で所望の気孔率をもつ発泡体を得ることができる。それ以上の圧力を得るために設備コストが高くなり、不経済である。従って、ガスの全圧力は1～500気圧の範囲内とする。

【0014】図1にFe中の水素の溶解度を、種々の水素圧力の場合について例示する。Feの融点は1539°C程度であり、水素溶解度は固体Feでは水素圧力の大小に依らず小さいが、液体Feになると急激に大きくなる。しかも、液体Fe中の水素溶解度は水素圧力が大きくなるほど大きくなることがわかる。従って、固体Fe

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中に多量の水素ガスを残留させるためには、液体状態のFeに加えていた水素圧力をそのまま保持して凝固せなければならない。

【0015】溶湯中のガスの溶解度は、ガス-溶湯物質の組み合わせに応じて、温度およびガスの圧力により定まる。そして固体内に残留するガス量は主に上記組み合わせとガス圧力により決まるので、これにより気孔率を調整することができる。

【0016】溶湯中がFeでガス種が水素の場合に限らず、溶湯が金属またはセラミックスでガスが水素、窒素および酸素の場合には上記と同じ傾向の挙動をする。従って、(イ)の条件が必要である。

【0017】(ロ)ガス種を水素、窒素および酸素の内から少なくとも一種を選び、且つ溶湯を攪拌しながら冷却・凝固させると：溶湯に溶解させるガス種は、当該ガスを含有した溶湯（金属溶湯またはセラミックス溶湯）が凝固するときに、共晶反応を起こすことが必要である。溶湯が凝固するときに共晶反応を起こす場合には、当該溶湯物質の固相と当該ガス相とがミクロ的に層状に析出する。所謂共晶組織を形成する場合には、凝固時、即ち、当該溶湯が純金属等純物質または全率固溶体を形成する多元系合金等多元系物質（以下、「純物質等」という）の場合は融点において、全率固溶体を形成しない多元系合金等多元系物質（以下、「多元系物質等」という）の場合には固液が共存する液相線温度以下、固相線温度以上の温度域において、溶湯を上方および側面から冷却することなく、下方からのみ冷却することにより気孔が下から上に延びた一方向凝固体を得ることができる。

【0018】水素、窒素および酸素は、Fe、Ni、Cu、AlおよびMo等の金属やアルミナおよびマグネシアと共に反応を起こすガスである。図2に、Cu-H系の二元系平衡状態図の模式図を示す。同図において、MはCuを表す。本発明の方法をCu-H系に適用し、溶湯内の小領域に注目すると、同図中、直線Bに沿って溶湯温度をゆっくり下げていき、共晶温度P点になると温度低下が停滞し、球状気泡が固液界面に形成されて凝固の進行につれて上方に長く成長し、凝固が完了し、再度温度が低下していき、Cuの発泡金属が得られる。

【0019】図3に、本発明による溶湯の凝固過程におけるミクロ状態模式図を示す。融点または凝固温度において共晶反応を起こし、且つ一方向凝固をさせるので、液相の中に多数の柱状のガス相Gと固相Sとが析出しそれぞれが上方に成長する。ガス相Gの形態は表面張力の影響で円筒状に伸び、周囲が固相で埋めつくされる。

【0020】しかしながら、共晶反応以外の凝固組織を形成するガス種の場合には、凝固時に固相とガス相とがミクロ的に共存せずマクロ的に二相に分離する。従って、凝固体内部に気泡を形成させることが困難である。

【0021】(ハ)鋳型の温度を、当該金属またはセラ

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ミックスのそれぞれの融点 - 50 °C以上、融点 + 50 °C以下の範囲内に予熱すること：鋳型としては熱伝導性を確保することができる材質のものを使用し、必要に応じて冷却する。鋳型の温度は溶湯が純物質等の場合には融点 - 50 °C未満、多元系物質等の場合には液相線温度 - 50 °C未満の温度では、凝固核が鋳型壁で多数発生し、一方向凝固組織を得られない。一方、鋳型の温度がそれぞれ、融点または液相線温度 + 50 °C超えの温度では、凝固開始までに時間を要し、生産効率が低下したり鋳型寿命が短くなったりする。従って、鋳型を溶湯の融点または液相線温度 - 50 °C以上、融点または液相線温度 + 50 °C以下に予熱することが必要である。

【0022】(ニ) 金属またはセラミックス中に均一に方向性気孔を形成させ、気孔の直径 = 5 μm ~ 10 m m、気孔率 = 5% ~ 98%であること：気孔の形態が円柱状的に方向性を持つと、軽量構造部材や通気材にとって好都合であり、高強度なシャフトやフィルター組体といった用途に適する。

【0023】溶湯の温度およびガス圧力を、金属 - ガス系またはセラミックス - ガス系の種類に合わせて適宜選択することによりガスの溶解量を制御することができる（例えば、図1参照）。従って、発泡金属および発泡セラミックスの気孔の大きさおよび気孔率を制御することができる。気孔径は 5 μm 未満では、通気性が悪くなり、一方、10 mm より大きくなると材料強度を確保するのが困難になる。従って、気孔径は 5 μm ~ 10 mm の範囲内とする。溶湯の冷却速度が大きいほど小さい径の気孔が得られ、冷却速度が小さいほど気孔は成長するので大きい径の気孔が生成する。

【0024】また気孔率が 10% 未満では軽量性、通気性に劣り、一方、98% を超えると材料強度を確保するのが困難である。従って、気孔率は 5% ~ 98% の範囲内とする。溶湯内の気泡率が高くなると、溶湯の表面張力により気泡の膜が破裂して、気孔同士が連通したいわゆるオープンセルができる。オープンセルの形成は溶湯の粘度に依存するので、追道しない独立孔を形成させるときは、Ca や Mg 等を添加して増粘してやる。

【0025】(ホ) 鋳型の上面および側面からの抜熱を防止し、鋳型の下面からのみ抜熱をし、溶湯を凝固させること：方向性気孔を形成させるためには、一方向凝固組織を形成させることが必要であることは上述したとおりである。下方から冷却するのは、溶湯（液体）中に生成する結晶核（固体）は溶湯より密度が大きいので沈降する。従って、下方から凝固を行させないと、気泡を

均一に上方に延ばすことができない。従って、鋳型の冷却は下方向からに限定しなければならない。なお、冷却は窒素やアルゴン等のガス、または、ミストや水等を鋳型に吹き付けて行なう。

【0026】(ヘ) 溶湯に発泡核となる微細粒子を添加すること：気孔の分布を調整するために、溶湯の融点または液相線温度よりも融点が高い炭化物、窒化物あるいは酸化物等の微細粒子を適宜添加することが望ましい。これらの微細粒子は気孔の発生核となり、気孔の分布を

10 均一にするからである。

【0027】

【実施例】次に、この発明の発泡体の製造方法を、実施例によって更に詳細に説明する。図4に、実施例および比較例の方法を試験するため用いた溶解・鋳造装置の概略断面図を示す。装置全体が高圧容器1の中に入っている。溶解炉2により各種金属またはセラミックスを溶解する。得られた溶湯4にガス添加管5よりボーラスレンガ6を通って水蒸、窒素または酸素ガスを適宜吹き込みながら高圧容器1内の圧力を所定圧力まで高めて当該ガスを添加する。このようにして所定濃度のガスを溶解させた溶湯4を取容した溶解炉2を傾斜し、タンディッシュ7を経由して鋳型8に注入する。注入後は上部からの抜熱を防ぐために断熱レンガ15で鋳型8上部を覆う。鋳型8はヒーター3'により予め適温に加熱しておく。一方、鋳型3の下部に冷却媒体11を吹きつけ、鋳型下部から上方に向かって一方向に冷却すると、凝固金属またはセラミックス相とガス相が上方に成長する。冷却媒体11によって鋳型8に振動を与えると、凝固核が溶湯面に発生しやすないので、鋳型はしっかりと固定するのが望ましい。高圧容器1内のガス圧力は凝固完了まで上記所定圧力に保持し、溶湯の冷却・凝固時に溶湯からガスが抜け出すのを抑制する。

【0028】上記試験装置を用い上記方法により発泡金属および発泡セラミックスを製造した。表1に、本発明の範囲内である実施例No.1 ~ 10 および本発明の範囲外である比較例No.1 ~ 2 の各発泡体の製造条件、および得られた発泡体の性状（気孔形態、気孔径および気孔率）を示す。なお、各溶湯の融点（または液相線）+ 50 °Cから融点（または液相線）- 250 °Cまでの温度区間を、0.01 ~ 100 °C / sec の平均冷却速度で冷却した。

【0029】

【表1】

(5)

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7

8

	no	溶湯種類	添加ガス	ガス添加温度(℃)	ガス圧力(kPa)	添加微粒子	铸型温度(℃)	冷却媒体	気孔形態	気孔径	気孔率(%)
実施例	1	Ni	H	1000	50	—	1400	ミスト	柱状	0.5 mm	90
	2	Ni	H	1350	1.1	—	1420	空気	・	0 mm	50
	3	Ni	H	1500	460	TiC	1450	水	・	7 μm	38
	4	Fe	O	1100	10	—	980	空気	・	70 μm	63
	5	Al	H	700	150	—	640	空気	・	1 mm	25
	6	Fe-10Mn	N	1650	250	—	1450	空気	・	0.5mm	95
	7	Cu	H	1100	20	Al ₂ O ₃	1050	ミスト	・	30 μm	75
	8	チタン鋼	N+H	1600	100	TiN	1500	空気	・	1.2mm	80
	9	Al ₂ O ₃	H	2200	150	—	2000	空気	・	0.7mm	65
	10	Al ₂ O ₃	H	2900	200	—	2800	空気	・	0.3mm	75
比較例	1	Fe	H	1600	25	—	1400	水	柱状混入	30 μm	70
	2	Ni	H	1550	0.8	—	1430	空気	柱状	0.2mm	45

【0030】実施例No.1においては、1800℃のNi溶湯に50気圧で水素を添加し、これを1400℃に均一に予熱した铸型に铸込んだ。铸込み後铸型上部を断熱カバーで覆い、铸型の底面に水を微細な粒子としたミストを吹付けて一方向から冷却し完全凝固させた。これによって直径(短径)0.5mmの柱状に成長した気泡を有し、気孔率90%の発泡ニッケルを得ることができた。この発泡ニッケルの気孔の形態および分布状態の模式図を図5に示す。この発泡ニッケルを厚さ0.8mmの板にスライス切断してNi-OH電池の正極に使用した。これは従来品より安価であり、且つ気孔が表裏に貫通しているためNi(OH)₂の充填もスムーズであり、電圧低下の小さい優れた電極性能を示した。

【0031】実施例No.2～10においては、冷却媒体を一部変更し、実施例No.1に進じた方法で発泡体を製造した。但し、実施例No.3、7および8では、溶湯にそれぞれTiC、Al₂O₃およびTiNの微粒子を添加した。また、溶湯の種類および添加ガスの種類を一部変更した。その他の製造条件は表1に示した通りである。いずれも柱状の気孔を有し、所望の柱状の発泡体を得ることができた。

【0032】これに対して比較例No.1では、铸型温度が溶湯金属、鉄の融点-50℃より低かったため、铸型壁から結晶粒が成長し、発泡鉄の一部に粒状の気孔が混入して形成された。

【0033】比較例2では、水素ガス添加圧力が低く本

発明の範囲外であったため、発泡ニッケルの気孔率が50%未満であった。

【0034】

【発明の筋】以上述べたように、この発明によれば、従来製造が困難であったり、コストが高かったりした高融点の金属の発泡体、軽量性および通気性において十分満足することができなかったセラミックスの発泡体、並びに、多種類の金属、合金およびセラミックスの発泡体であって方向性気孔を有するものを、高圧下における溶解、铸造および凝固という簡単な工程により簡単に製造する方法を提供することができ、工業上有用な効果がもたらされる。

【図面の簡単な説明】

【図1】柱の水素圧力の場合の、Feの温度と水素の溶解度との関係を示すグラフである。

【図2】Cu-H系の二元系平衡状態図の模式図である。

【図3】本発明による溶湯の凝固過程における内部のマイクロ的模式図である。

【図4】実施例および比較例の方法を試験するために用いた溶解・铸造装置の概略横断面図である。

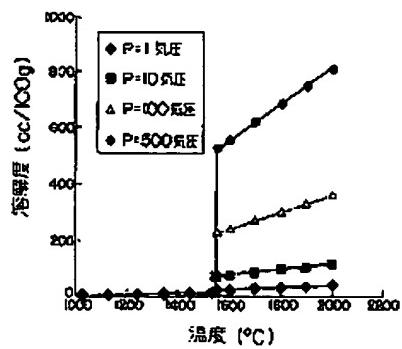
【図5】本発明の方針により得られた発泡ニッケルの気孔の形態および分布状態を模式的に示す一部断面切欠き図である。

【符号の説明】

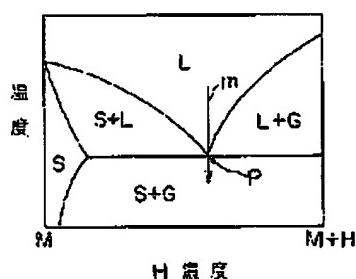
50 1 高圧容器

(5)	特開平10-158761
9	10
2 溶解炉	* 12 冷却媒体供給管
3, 3' ヒーター	13 冷却媒体排出管
4, 4', 4'' 浸漬	14 ガス導気管
5 ガス添加管	15 断熱レンガ
6 ポーラスレンガ	16 柱状気孔
7 タンディッシュ	17 ニッケル金属
8 鑄型	L 液体
9 一方向凝固金属	S 固体
10 気孔	G 気体
11 冷却媒体	
	*10

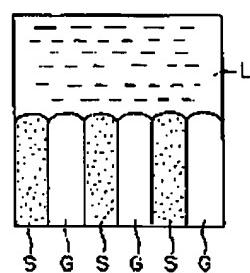
【図1】



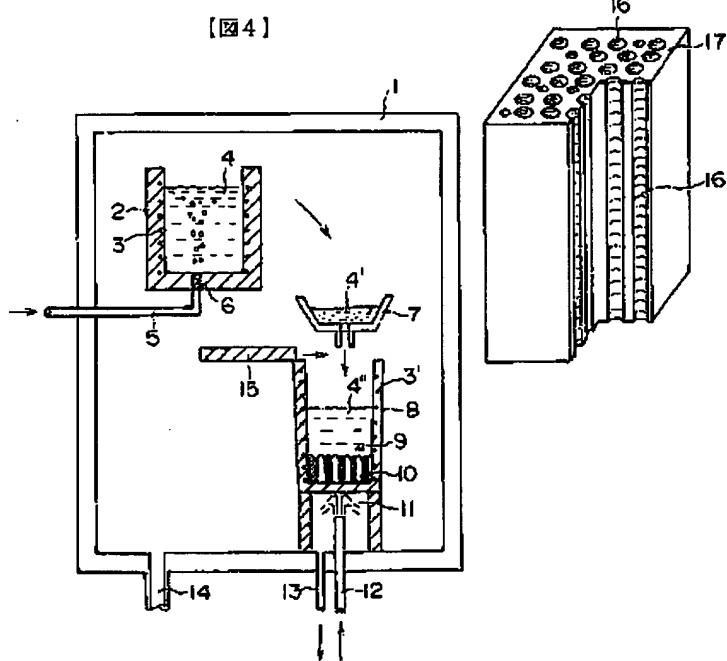
【図2】



【図3】



【図5】



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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of the foam which has the directivity pore characterized by consisting of a process of following (a) - (e).

(a) (b) b [the process which dissolves a metal or the ceramics into a fusion furnace, and obtains a molten metal, and] Rank second. By consisting only of at least one sort of gas among hydrogen, nitrogen, and oxygen gas to said molten metal, and applying the total pressure of the gas concerned within the limits of one to 500 atmospheric pressure (d) d [the process which heats beforehand the process which dissolves said gas in said molten metal, and (c) mold to temperature with a melting point / of said metal or said ceramics / each / of -50 degrees C or more /, and a melting point of +50 degrees C or less within the limits, and] Rank second. The total pressure of said gas added to said mold which said temperature preheated at the process which casts said molten metal, and the (e) aforementioned molten metal has been held with the total pressure of said gas added to said molten metal held. The process which has the directivity pore of 5 micrometers - 10mm of minor axes prolonged for a long time up by preventing cooling from the top face and side face of said mold, carrying out cooling only from the underside of said mold, and making a molten metal solidify, and foam of 50 - 98% of porosity is made to carry out one direction coagulation.

[Claim 2] The manufacture approach of the foam which has further the directivity pore characterized by adding the process which adds the very fine particle which serves as a foaming nucleus at a molten metal at the process of invention according to claim 1.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of a foam metal (an alloy is included) and the foaming ceramics.

[0002]

[Description of the Prior Art] A foam metal and porous ceramics are a melted kind which made the countless air bubbles by foaming remain in a metal, and a kind of the ceramics which made countless pore form into the ceramics, respectively, and its all are lightweight, and they are the ingredients excellent in permeability and a filtration function.

[0003] There is the approach of ** of a degree and ** as an approach of manufacturing such a foam metal.

** By the manufacture approach this gentleman method by electroplating, use urethane foam as foaming resin, in order to perform electric conduction processing to this, apply carbon, and perform nickel plating for this in an electric plating bath. Calcining of after nickel plating is carried out at 600 degrees C, it incinerates urethane foam, and returns it in a 900-degree C hydrogen air current further. Although electric conduction processing is unnecessary since a pitch based carbon fiber is conductivity when using the felt of a pitch based carbon fiber for a foaming base material, it is manufactured through the process of reduction one by one by the washing [of the felt], electroplating, and calcining following ** like the above-mentioned example.

[0004] Thus, when the obtained foam metal is used as a substrate of the electrode of nickel-Cd and a Ni-H battery, it is nickel (OH)₂. Since it can be filled up with negative-electrode active materials, such as positive active material, Cd, and a hydrogen storing metal alloy, so much in pore, miniaturization of a cell and high capacity-ization can be attained.

[0005] ** The manufacture approach this gentleman method by casting is adopted by manufacture of a foam metal with the low melting point like aluminum. That is, air is blown into a metal molten metal, and after adding calcium etc. and making viscosity increase, a foaming agent is added in the temperature near [the] the melting point. As a foaming agent, the hydride which generates gas, and the natural mineral containing water are used. It is made to solidify, since gas air bubbles are generated shortly after adding a foaming agent to a metal molten metal, agitating a molten metal quickly with an agitator and distributing air bubbles.

[0006] On the other hand, there is an approach by ** sintering process as an approach of manufacturing the porous body of the ceramics. As for this approach, it is common to prepare the ceramics to a predetermined size range, and to sinter and manufacture the obtained ceramic powder.

[0007]

[Problem(s) to be Solved by the Invention] However, there is the following problem in the manufacture approach of the above-mentioned ** - **, respectively. That is, the manufacture approach by ** electroplating consists of many processes, as mentioned above. Therefore, since the foam metal plate which slices thinly the foam metal manufactured by this approach, and is made became expensive, it had

become the cause which bars the spread of foam metals.

[0008] ** Since the foaming agent generated gas at comparatively low temperature when based on casting, foam manufacture of the metal which has the high melting point which can manufacture only a metal with the low melting point like aluminum, but exceeds 1000 degrees C like nickel or iron was difficult the former. Moreover, when manufacturing the foam of a metal with the high melting point, the high matter of a generation-of-gas elevated temperature must be used like a titanium hydride as a foaming agent. However, such a foaming agent is expensive and a manufacturing cost becomes high.

[0009] ** With the foaming ceramics by the sintering process, only that whose porosity is about 50% could be manufactured, but the problem was in lightweight nature and permeability. Therefore, the object of this invention solves the problem mentioned above, manufactures it according to a suitable production process more cheaply than before, and conventionally, since foam is expensive in manufacture being difficult, manufactures the foam of the high-melting metal which was high as for the manufacturing cost by the simple approach, and manufactures it more cheaply. And it is in offering the approach that the highly efficient foaming [which was not obtained conventionally] ceramics which was lightweight and was excellent in permeability can be manufactured simple.

[0010]

[Means for Solving the Problem] this invention person etc. was a completely new approach, repeated research wholeheartedly that the approach of manufacturing the foam metal and foaming ceramics which can control porosity in the magnitude of pore and directivity, and a list simple should be developed, and acquired the following knowledge from a viewpoint mentioned above. That is, it found out that the foam metal and foaming ceramics of the description for which it wishes could be manufactured by making it solidify, controlling cooling agitating a molten metal in the condition [fusing the matter concerned, dissolving gas under the suitable high voltage for the obtained molten metal, and having dissolved gas].

[0011] This invention is made based on the above-mentioned knowledge, and the manufacture approach of foam according to claim 1 has the description to consist of a process of following (a) - (e).

(a) (b) b [the process which dissolves a metal or the ceramics into a fusion furnace, and obtains a molten metal, and] Rank second. By consisting only of at least one sort of gas among hydrogen, nitrogen, and oxygen gas to a molten metal, and applying the total pressure of the gas concerned within the limits of one to 500 atmospheric pressure (d) d [the process which heats beforehand the process which dissolves gas in a molten metal, and (c) mold to temperature with a melting point / of a metal or the ceramics / each / of -50 degrees C or more /, and a melting point of +50 degrees C or less within the limits, and] Rank second. The total pressure of the gas added to the mold which the above-mentioned temperature preheated at the process which casts a molten metal, and the (e) molten metal has been held with the total pressure held applied to the molten metal. The process which has the directivity pore of 5 micrometers - 10mm of minor axes prolonged for a long time up by preventing cooling from the top face and side face of mold, carrying out cooling only from the underside of mold, and making a molten metal solidify, and foam of 50 - 98% of porosity is made to carry out one direction coagulation.

[0012] The manufacture approach of foam according to claim 2 has the description to add further the process which adds the very fine particle which serves as a foaming nucleus at a molten metal to invention according to claim 1.

[0013]

[Embodiment of the Invention] Next, the reason limited as the manufacture approach of this invention was mentioned above is explained.

(b) It casts and cools to predetermined mold and it is made to solidify holding within the limits of total pressure =1 - 500 atmospheric pressure of the gas to a molten metal, and holding the pressure. : dissolving a metal or the ceramics by the predetermined approach first, other gas makes at least the gas ambient atmosphere which is not included substantially including a kind of gas among nitrogen, oxygen, and hydrogen gas to the molten metal subsequently obtained. Within the limits of one to 500 atmospheric pressure, the total pressure of this gas ambient atmosphere dissolves the gas concerned. The total pressure of gas has few amounts of dissolution of gas with less than one atmospheric pressure, and

it is difficult to obtain the foam of high porosity. On the other hand, the foam which has desired porosity with the total pressure to 500 atmospheric pressures can be obtained. In order to obtain the pressure beyond it, facility cost becomes high, and it is uneconomical. Therefore, total pressure of gas is made into within the limits of one to 500 atmospheric pressure.

[0014] The solubility of the hydrogen in Fe is illustrated about the case of various hydrogen pressure force to drawing 1. The melting point of Fe is about 1539 degrees C, hydrogen solubility does not depend on the size of the hydrogen pressure force by Solid-state Fe, but although it is small, if it becomes Liquid Fe, it will become large rapidly. And it turns out that the hydrogen solubility in Liquid Fe becomes so large that the hydrogen pressure force becomes large. Therefore, in order to make a lot of hydrogen gas remain in Solid-state Fe, the hydrogen pressure force which was being applied to Fe of a liquid condition must be held as it is, and must be made to solidify.

[0015] The solubility of the gas to the inside of a molten metal becomes settled with temperature and the pressure of gas according to the combination of the gas-molten metal matter. And since the capacity which remains in a solid-state is mainly decided by the above-mentioned combination and gas pressure, thereby, porosity can be adjusted.

[0016] Not only when a molten metal kind is [a type of gas] hydrogen in Fe but when it is gas and molten metals are hydrogen, nitrogen, and oxygen with a metal or the ceramics, behavior of the same inclination as the above is carried out. Therefore, the conditions of (b) are required.

[0017] (b) Cooling and coagulation of are done choosing a kind for a type of gas from at least among hydrogen, nitrogen, and oxygen, and agitating a molten metal. : the type of gas dissolved in a molten metal needs to cause an eutectic reaction, when the molten metal (a metal molten metal or ceramic molten metal) containing the gas concerned solidifies. When a molten metal solidifies, in causing an eutectic reaction, the solid phase and the gas phase concerned of the molten metal matter concerned form the so-called eutectic structure which deposits in the shape of a layer in micro. In forming eutectic structure, in the case of plural system matter ("henceforth a pure substance etc."), such as the time of coagulation, i.e., the plural system alloy with which the molten metal concerned forms pure substances, such as a pure metal, or a complete solid solution, it sets to the melting point. In the temperature region below the liquidus-line temperature in which solid-liquid carries out a coexistence layer in the case of plural system matter ("henceforth the plural system matter etc."), such as a plural system alloy which does not form a complete solid solution, and beyond solidus-line temperature Pore can acquire from the bottom the one direction coagulation object prolonged upwards by cooling only from a lower part, without cooling a molten metal from the upper part and a side face.

[0018] Hydrogen, nitrogen, and oxygen are gas which causes a metal, an alumina and a magnesia, and eutectic reactions, such as Fe, nickel, Cu, aluminum, and Mo. drawing 2 -- the duality of a Cu-H system -- the mimetic diagram of a system equilibrium diagram is shown. In this drawing, M expresses Cu. If molten metal temperature is slowly lowered along with the straight line m among this drawing if the approach of this invention is applied to a Cu-H system and the small region in a molten metal is observed, and it becomes P eutectic temperature, temperature lowering will stagnate, and spherical air bubbles are formed in a solid-liquid interface, it grows up for a long time up along with progress of coagulation, coagulation is completed, temperature falls again, and the foam metal of Cu is obtained.

[0019] The microstate mimetic diagram in the coagulation process of the molten metal by this invention is shown in drawing 3. Since a lifting and one direction coagulation are carried out for an eutectic reaction in the melting point or coagulation temperature, into the liquid phase L, many column-like the gas phases G and solid phase S deposit, and each grows up. The gestalt of the gas phase G is prolonged in the shape of a cylinder under the effect of surface tension, and a perimeter is filled with solid phase.

[0020] However, in the case of the type of gas which forms solidification structure other than an eutectic reaction, solid phase and a gas phase do not live together in micro at the time of coagulation, but it separates into a two phase in macro. Therefore, it is difficult to make air bubbles form in the interior of a coagulation object.

[0021] (c) The temperature of mold is beforehand heated to within the limits with a melting point [of the metal concerned or the ceramics / each / of -50 degrees C or more], and a melting point of +50

degrees C or less. : use the thing of construction material which can secure thermal conductivity as mold, and cool if needed. For the temperature of mold, in the case of a pure substance etc., a molten metal is the melting point. - In the case of less than 50 degrees C, the plural system matter, etc., at temperature with a liquidus-line temperature of less than -50 degrees C, many coagulation nuclei occur with a mold wall, and one direction solidification structure is not obtained. On the other hand, at the temperature which the temperature of mold exceeds the melting point or the liquidus-line temperature of +50 degrees C, respectively, time amount is required by coagulation initiation, productive efficiency falls or a mold life becomes short. Therefore, it is required to heat mold beforehand to the melting point or the liquidus-line temperature of -50 degrees C or more, the melting point, or liquidus-line temperature of +50 degrees C or less of a molten metal.

[0022] (d) What directivity pore is made to form into a metal or the ceramics at homogeneity, and is been diameter =5micrometer-10mm of pore, and porosity =50-98% : when the gestalt of pore has directivity in cylindrical, it is convenient for a light-construction member or aeration material, and suitable for applications, such as a high intensity shaft and filter support.

[0023] The amount of dissolutions of gas is controllable by choosing the temperature and gas pressure of a molten metal suitably according to the class of a metal-gas system or ceramic-gas system (for example, refer to drawing 1). Therefore, the magnitude and the porosity of pore of a foam metal and the foaming ceramics are controllable. If permeability worsens and a pore diameter becomes larger than 10mm on the other hand in less than 5 micrometers, it will become difficult to secure material strength. Therefore, a pore diameter is made into within the limits of 5 micrometers - 10mm. The pore of such a small path that the cooling rate of a molten metal is large is obtained, and since pore grows, the pore of a large path generates it, so that a cooling rate is small.

[0024] Moreover, if porosity is inferior to lightweight nature and permeability at less than 50% and it exceeds 98% on the other hand, it is difficult to secure material strength. Therefore, porosity is made into 50 - 98% of within the limits. If the void volume in a molten metal becomes high, the film of air bubbles will explode with the surface tension of a molten metal, and the so-called open cell which pores opened for free passage will be made. Formation of an open cell adds and thickens calcium, Mg, etc., when making the independent hole which is not open for free passage form, since it is dependent on the viscosity of a molten metal.

[0025] (e) Cooling from the top face and side face of mold is prevented, cooling is carried out only from the underside of mold, and a molten metal is made to solidify. : in order to make directivity pore form, it is as having mentioned above that it is required to make one direction solidification structure form. Since the consistency is larger than a molten metal, the crystalline nucleus (solid-state) which cooling from a lower part generates in a molten metal (liquid) sediments. Therefore, unless it advances coagulation from a lower part, air bubbles cannot be extended up to homogeneity. Therefore, cooling of mold must be limited from down. In addition, cooling sprays gas, such as nitrogen and an argon, Myst, water, etc. on mold, and performs them.

[0026] (**) in order to adjust distribution of the thing:pore which adds the very fine particle used as a foaming nucleus to a molten metal -- a charcoal fire with the melting point higher than the melting point or liquidus-line temperature of a molten metal -- it is desirable to add suitably very fine particles, such as an object, a nitride, or an oxide. It is because these very fine particles serve as a generating nucleus of pore and distribution of pore is made into homogeneity.

[0027]

[Example] Next, an example explains the manufacture approach of the foam this invention to a detail further. Outline drawing of longitudinal section of dissolution / casting equipment used for drawing 4 in order to examine the approach of an example and the example of a comparison is shown. As for close, the whole equipment is in a high pressure vessel 1. Various metals or the ceramics is dissolved with a fusion furnace 2. The pressure in a high pressure vessel 1 is suitably raised for hydrogen, nitrogen, or oxygen gas to the obtained molten metal 4 from the gas addition tubing 5 to a predetermined pressure with an entrainment through the porous brick 6, and the gas concerned is added. Thus, the fusion furnace 2 in which the molten metal 4 in which the gas of predetermined concentration was dissolved

was held is tilted, and it pours into mold 8 via tundish 7. After impregnation is a wrap about the mold 8 upper part with heat insulating brick 15, in order to prevent cooling from the upper part. Mold 8 is beforehand heated to optimal temperature by heater 3'. On the other hand, if a cooling medium 11 is sprayed on the lower part of mold 3 and it cools from the mold lower part to an one direction toward the upper part, a coagulation metal phase or a ceramic phase, and a gas phase will grow up. If an oscillation is given to mold 8 with a cooling medium 11, since it will be easy to generate a coagulation nucleus in a molten metal side, as for mold, fixing firmly is desirable. The gas pressure in a high pressure vessel 1 is held to the above-mentioned predetermined pressure till the completion of coagulation, and it controls that gas slips out from a molten metal at the time of cooling and coagulation of a molten metal.

[0028] A foam metal and the foaming ceramics were manufactured by the above-mentioned approach using the above-mentioned testing device. Example No.1-10 which are within the limits of this invention, the manufacture conditions of each foam of example No. of comparison1-2 that this invention is out of range, and the acquired description (a pore gestalt, a pore diameter, and porosity) of foam are shown in a table 1. In addition, the temperature section from the melting point of +50 degrees C of each molten metal (or liquidus line) to the melting point (or liquidus line) of -250 degrees C was cooled with the average cooling rate of 0.01-100 degrees C/sec.

[0029]

[A table 1]

	No	溶湯種類	添加ガス	ガス添加温度 (°C)	ガス圧力 (atm)	添加微粒子	鋳型温度 (°C)	冷却媒体	気孔形態	気孔径	気孔率(%)
実施例	1	Ni	H	1800	50	—	1400	ミスト	柱状	0.5 mm	90
	2	Ni	H	1550	1.1	—	1420	空気	"	8 mm	50
	3	Ni	H	1500	460	TiC	1450	水	"	7 μm	98
	4	Ag	O	1100	10	—	960	窒素ガス	"	70 μm	65
	5	Al	H	700	150	—	640	空気	"	1 mm	85
	6	Fe-10%Mn	N	1650	250	—	1450	窒素ガス	"	0.5mm	95
	7	Cu	H	1100	20	Al ₂ O ₃	1060	ミスト	"	30 μm	75
	8	ステンレス 鋼	N + H	1600	100	TiN	1500	窒素ガス	"	1.2mm	80
	9	Al ₂ O ₃	H	2200	150	—	2000	窒素ガス	"	0.7mm	65
	10	MgO	H	2900	200	—	2800	窒素ガス	"	0.3mm	75
比較例	1	Fe	H	1600	25	—	1400	水	粒状混入	30 μm	70
	2	Ni	H	1550	0.8	—	1430	空気	柱状	0.2mm	45

[0030] In example No.1, hydrogen was added with 50 atmospheric pressures to 1800-degree C nickel molten metal, and it cast to the mold which preheated this at 1400 degrees C at homogeneity. It sprayed, and full coagulation of Myst which made water the detailed particle for the mold upper part after casting on the base of a bonnet and mold with the insulation cover was cooled and carried out from the one direction. By this, it has the air bubbles which grew with a diameter (minor axis) of 0.5mm in the shape of a column, and foaming nickel of 90% of porosity was able to be obtained. The mimetic diagram of

the gestalt of the pore of this foaming nickel and a distribution condition is shown in drawing 5. Slice cutting was carried out and this foaming nickel was used for the plate with a thickness of 0.8mm at the positive electrode of a Ni-H battery. Since it is conventionally cheaper than elegance and pore has penetrated on the front reverse side, this is nickel (OH)2. Restoration is also smooth and the small outstanding electrode engine performance of sag was shown.

[0031] In example No.2-10, the partial change of the cooling medium was carried out, and foam was manufactured by the approach according to example No.1. However, at example No.3, and 7 and 8, they are TiC and aluminum 2O3 to a molten metal, respectively. And the particle of TiN was added. Moreover, the partial change of the class of molten metal and the class of addition gas was carried out. Other manufacture conditions are as having been shown in a table 1. All have column-like pore and were able to obtain the foam of desired description.

[0032] On the other hand, in example No.of comparison 1, since mold temperature was lower than the melting point of -50 degrees C of a molten metal metal and iron, crystal grain grew from the mold wall, and grain-like pore was mixed and formed in some foaming iron.

[0033] In the example 2 of a comparison, since the hydrogen gas addition pressure was low and this invention's was out of range, the porosity of foaming nickel was less than 50%.

[0034]

[Effect of the Invention] As stated above, according to this invention, conventionally, manufacture is difficult or The foam of the ceramics which was not able to be enough satisfied in the foam, the high-melting metaled lightweight nature, and the high-melting metaled permeability whose cost was high, A list can be provided with the approach of manufacturing simple what is foam of the metal of varieties, an alloy, and the ceramics, and has directivity pore according to the easy process of the dissolution under high voltage, casting, and coagulation, and useful effectiveness is brought to it on industry.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the graph which shows the relation between the temperature of Fe in the case of various hydrogen pressure force, and the solubility of hydrogen.

[Drawing 2] the duality of a Cu-H system -- it is the mimetic diagram of a system equilibrium diagram.

[Drawing 3] It is the micro mimetic diagram of the interior in the coagulation process of the molten metal by this invention.

[Drawing 4] It is outline drawing of longitudinal section of dissolution / casting equipment used in order to examine the approach of an example and the example of a comparison.

[Drawing 5] the gestalt and distribution condition of pore of foaming nickel which were acquired by the approach of this invention are shown typically -- it is cross-section notch drawing a part.

[Description of Notations]

1 High Pressure Vessel

2 Fusion Furnace

3 3' Heater

4, 4', 4" Molten metal

5 Gas Addition Tubing

6 Porous Brick

7 Tundish

8 Mold

9 One Direction Coagulation Metal

10 Pore

11 Cooling Medium

12 Cooling-Medium Supply Pipe

13 Cooling-Medium Exhaust Pipe

14 Flueing Tubing

15 Heat Insulating Brick

16 Pillar-shaped Pore

17 Nickel Metal

L Liquid

S Solid-state

G Gas

[Translation done.]

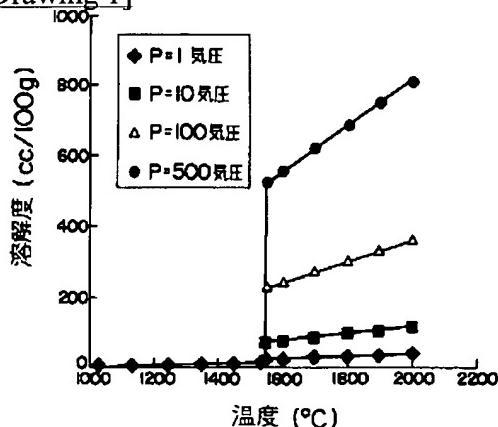
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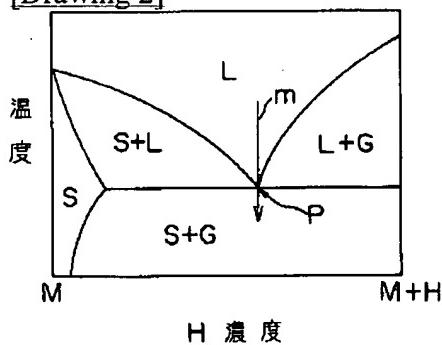
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DRAWINGS

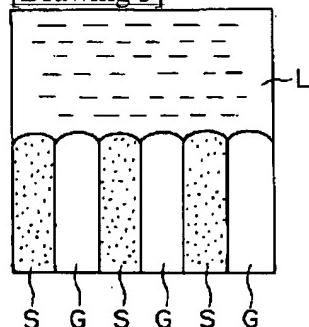
[Drawing 1]



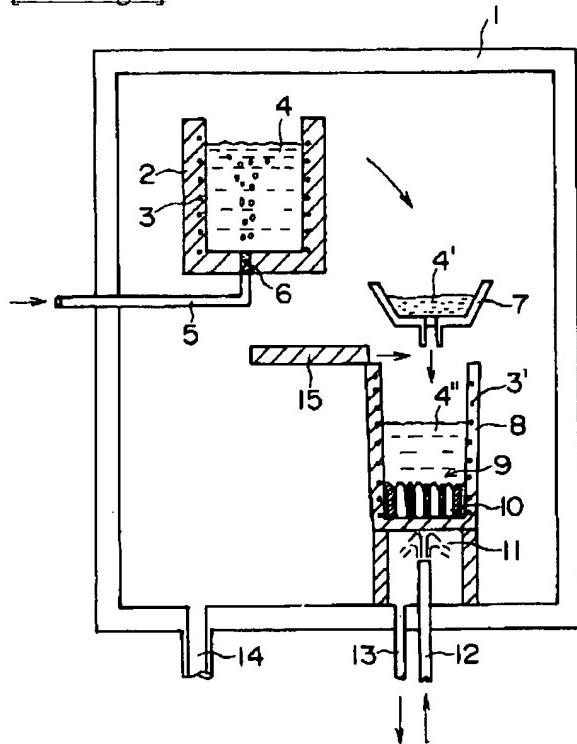
[Drawing 2]



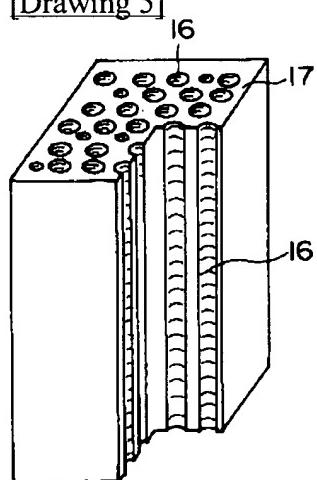
[Drawing 3]



[Drawing 4]



[Drawing 5]



[Translation done.]